

**Standard Operating Procedure
for Chloride and Silica in Lake Water
(Lachat Method)**

LG205

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Standard Operating Procedure for Chloride and Silica in Lake Water (Lachat Method)

1.0 SCOPE AND APPLICATION

- 1.1 This method covers the determination of chloride and silica in lake water.
- 1.2 The approximate working range is 0.03 - 30.0 mg Cl/L and 0.01 - 2.00 mg Si/L. The method detection limits are 0.030 mg Cl/L and 0.010 mg Si/L.

2.0 SUMMARY

- 2.1 Thiocyanate ion is liberated from mercuric thiocyanate by the formation of soluble mercuric chloride. In the presence of ferric ion, free thiocyanate ion forms the highly colored ferric thiocyanate, of which the absorbance is proportional to the chloride concentration. Ferric thiocyanate absorbs strongly at 480 nm. The calibration curve is non-linear.
- 2.2 Soluble silica species react with molybdate under acidic conditions to form a yellow silica molybdate complex. This complex is subsequently reduced with 1-amino-2-naphthol-4-sulfonic acid (ANSA) and bisulfite to form a heteropoly blue complex which has an absorbance maximum at 820 nm.

3.0 SAMPLE HANDLING AND PRESERVATION

- 3.1 Samples are collected in clean plastic containers and stored at 4°C.

4.0 INTERFERENCES

- 4.1 Chloride
 - 4.1.1 Substances which reduce Fe^{+3} to Fe^{+2} and Hg^{+3} to Hg^{+2} (e.g., sulfite, thiosulfate).
 - 4.1.2 Halides which also form strong complexes with mercuric ion (e.g., Br-, I-) give a positive result.
- 4.2 Silica
 - 4.2.1 The interference due to phosphate is reduced by the addition of oxalic acid. An 8" reaction coil after the oxalic acid may be substituted for the 4" coil if found to be necessary.
 - 4.2.2 Tannin and large amounts of iron or sulfides are interferences.
 - 4.2.3 Silica contamination may be avoided by storing samples, standards, and reagents in plastic containers.

5.0 APPARATUS

- 5.1 13 X 100 mm plastic test tubes.
- 5.2 Lachat QuikChem FIA 8000
 - 5.2.1 XYZ Sampler
 - 5.2.2 Chloride manifold (Lachat Method # 10-117-07-1-B)
 - 5.2.3 Silica manifold (Lachat Method # 10-114-27-1-A)
 - 5.2.4 Printer

6.0 REAGENTS AND STANDARDS

- 6.1 All reagents should be stored in the appropriate bottles and labeled with the following information:

Identity: (15 N Sodium hydroxide)

Concentration: (1000 mg Cl/L)

Date of Preparation: (mm/dd/yy)

Expiration Date: (mm/dd/yy)

Initials of Preparer: (MPY)

- 6.2 *Use reagent water for all solutions.*

- 6.3 Chloride

- 6.3.1 **Stock Mercuric Thiocyanate Solution:** In a 1-L volumetric flask, dissolve 4.17 g mercuric thiocyanate ($\text{Hg}(\text{SCN})_2$) in approximately 500 mL methanol. Dilute to the mark with methanol and invert to mix.

CAUTION: *Mercury is a very toxic metal! Wear gloves!*

- 6.3.2 **Stock Ferric Nitrate Reagent, 0.5 M:** In a 1-L volumetric flask dissolve 202.0 g ferric nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) in approximately 800 mL of reagent water. Add 25 mL concentrated nitric acid, dilute to the mark and to mix.

- 6.3.3 **Combined Color Reagent:** In a 500-mL volumetric flask, mix 75 mL Stock Mercuric Thiocyanate with 75 mL stock ferric nitrate reagent and dilute to the mark with reagent water and invert to mix.

- 6.4 Silica

- 6.4.1 **Molybdate Reagent:** In a 500-mL volumetric flask dissolve 20.0 g of ammonium molybdate tetrahydrate $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}]$ in approximately 400 mL of reagent water.

Add 8.0 mL of H₂SO₄(conc.), dilute to the mark and degas with helium. Store in plastic container. Discard if precipitate or blue color is observed.

6.4.2 **Oxalic Acid:** In a 500-mL volumetric flask, dissolve 50.0 g oxalic acid (HO₂CCO₂H·2H₂O) in approximately 450 mL of reagent water dilute to the mark and degas with helium. Store in plastic container. Do not refrigerate.

6.4.3 **ANSA Reducing Agent:** In a 100-mL volumetric flask dissolve 2.0 g sodium sulfite (Na₂SO₃) in approximately 80 mL of reagent water. Add 0.25 g of 1-amino-2-naphthol-4-sulfonic acid. Dissolve and dilute to the mark. Prepare a second solution by dissolving 15 g sodium bisulfite (NaHSO₃) in 300 mL of reagent water. In a dark plastic container mix the two solutions. Add 4 mL glycerol. Degas with helium. Store refrigerated and discard when it becomes dark.

6.5 Preparation of Standards

6.5.1 **Chloride Stock Calibration Standard (10,000 mg Cl/L):** In a 500-mL volumetric flask dissolve 8.24 g NaCl (dried at 105°C for 2 hours). Dilute to the mark with reagent water.

6.5.2 **Silica Stock Calibration Standard (1,000 mg Si/L):** Purchased commercially.

6.5.3 **Intermediate Chloride Calibration Standard (1,000 mg Cl/L):** To a 500-mL volumetric flask, add 50.0 mL 10,000 mg/L Chloride Stock Calibration Standard (6.5.1). Dilute to the mark.

6.5.4 **Intermediate Silica Calibration Standard (200 mg-Si/L):** To a 500-mL volumetric flask, add 100.0 mL of 1,000 mg Si/L Silica Stock Calibration Standard (6.5.2). Dilute to the mark.

6.5.5 **Combined Working Standards:** Prepare standards over the range of analysis. For the working range 0 - 30 mg Cl/L and 0 - 2.00 mg Si/L, the following standards may be used:

Standard ID	mL Chloride Intermediate Calibration Standard (6.5.3) Diluted to 1 L	mL Silica Intermediate Calibration Standard (6.5.4) Diluted to 1 L	Concentration mg Cl/L	Concentration mg Si/L
	0.0	-----	0.00	-
H	1.5	-----	1.50	-
G	3.0	-----	3.00	-
F	5.0	0.0	5.00	0.00
E	10.0	0.5	10.00	0.10
D	15.0	1.0	15.00	0.20
C	20.0	2.5	20.00	0.50
B	25.0	5.0	25.00	1.00
A	30.0	10.0	30.00	2.00

6.5.6 **Chloride High Check Control Standard Stock (1,730 mg Cl/L):** In a 1-L volumetric flask dissolve 3.6382 g KCl (dried at 105°C for 2 hours) and dilute to the mark.

- 6.5.7 **Chloride Low Check Control Standard Stock (560 mg Cl/L):** In a 1-L volumetric flask dissolve 1.1777 g KCL (dried at 105°C for 2 hour) and dilute to the mark.
- 6.5.8 **Silica Control Standard Stock (467 mg Si/L):** In a 1-L volumetric flask dissolve 3.13 g of Na₂SiF₆ and dilute to the mark.
- 6.5.9 **Silica Intermediate High Check Control Standard (46.7 mg Si/L):** To a 500-mL volumetric flask add 50 mL of Silica Control Standard Stock (6.5.8) and dilute to the mark.
- 6.5.10 **Silica Intermediate Low Check Control Standard (9.3 mg Si/L):** To a 500-mL volumetric flask add 10 mL of Silica Control Standard Stock (6.5.8) and dilute to the mark.
- 6.5.11 **Combined Laboratory Performance High Check:** In a 200-mL volumetric flask combine 2 mL of Chloride High Check Control Standard Stock (6.5.6) and 2 mL of Silica Intermediate High Check Control Standard (6.5.9) and dilute to the mark. The concentrations of the High Check are 17.3 mg Cl/L, 0.467 mg Si/L.
- 6.5.12 **Combined Laboratory Performance Low Check:** In a 200-mL volumetric flask, add 2 mL of Chloride Low Check Control Standard Stock (6.5.7) and 2 mL Silica Intermediate Low Check Control Standard (6.5.10) and dilute to the mark. The concentrations of the Low Check are 5.6 mg Cl/L and 0.093 mg Si/L.

7.0 PROCEDURE

- 7.1 Follow the Lachat Procedural SOP (Typical Daily Operation Section).

8.0 CALCULATIONS

- 8.1 The computer yields results directly in mg Cl/L and mg Si/L.

9.0 QUALITY CONTROL

- 9.1 Refer to the Chapter 2 Introduction for definitions of quality control samples and information regarding quality control procedures, such as QC sample IDs and labeling.
- 9.2 The minimum acceptable correlation coefficient ($r \leq 0.995$).

- 9.3 The following **Chloride** QC samples must be prepared and analyzed at the minimum frequency indicated.

QC Sample Type		Frequency	Acceptance Criteria
External	Field Reagent Blank (FRB)	One per basin ^a	0.0 ± 0.2 mg/L or less than one-tenth associated field sample concentrations, whichever is greater
	Field Duplicate (FD1)	One per basin ^a	Relative Percent Difference (RPD) $\leq 20\%$
	Lab Duplicate (LD1)	One per basin ^a	RPD $\leq 20\%$
Internal	Calibration	At the beginning of each batch	$r \leq 0.995$
	High Check Standard (CH)	At the beginning & end of each batch or 1 per 40 samples, whichever is more frequent	17.3 ± 1.2 mg/L
	Low Check Standard (CL)	At the beginning & end of each batch or 1 per 40 samples, whichever is more frequent	5.6 ± 0.6 mg/L
	Laboratory Reagent Blank (LRB)	At the beginning & end of each batch or 1 per 40 samples, whichever is more frequent	0.0 ± 0.2 mg/L
	Method Detection Limit (MDL)	Once per year and each time a significant change is made to the SOP	0.14 mg/L

^a A field duplicate, lab duplicate, and field reagent blank are collected with each group of 3, 4, or 5 stations depending on the lake. A Random Number Generator (RNG) is used to determine the stations and depths of these QC samples. Where basins are well defined, at least one of each is collected from each basin.

- 9.4 The following **Silica** QC samples must be prepared and analyzed at the minimum frequency indicated.

QC Sample Type		Frequency	Acceptance Criteria
External	Field Reagent Blank (FRB)	One per basin ^a	0.000 ± 0.015 mg/L or less than one-tenth associated field sample concentrations, whichever is greater
	Field Duplicate (FD1)	One per basin ^a	Relative Percent Difference (RPD) $\leq 20\%$
	Lab Duplicate (LD1)	One per basin ^a	RPD $\leq 20\%$
Internal	Calibration	At the beginning of each batch	$r \leq 0.995$
	High Check Standard (CH)	At the beginning & end of each batch or 1 per 40 samples, whichever is more frequent	0.467 ± 0.053 mg/L
	Low Check Standard (CL)	At the beginning & end of each batch or 1 per 40 samples, whichever is more frequent	0.093 ± 0.018 mg/L
	Laboratory Reagent Blank (LRB)	At the beginning & end of each batch or 1 per 40 samples, whichever is more frequent	0.000 ± 0.015 mg/L
	Method Detection Limit (MDL)	Once per year and each time a significant change is made to the SOP	0.01 mg/L

^a A field duplicate, lab duplicate, and field reagent blank are collected with each group of 3, 4, or 5 stations depending on the lake. A Random Number Generator (RNG) is used to determine the stations and depths of these QC samples. Where basins are well defined, at least one of each is collected from each basin.

9.5 Assessment

- 9.5.1 The analyst must compare analytical results to the acceptance criteria listed in Sections 9.3 and 9.4 to identify QC failures. If the results are outside the acceptance criteria, the analyst should first review their calculations for errors and if none are identified, they must follow the corrective action procedures listed in Section 9.6.

9.6 Corrective Actions

- 9.6.1 Corrective action procedures will often be handled at the bench level by the analyst, who reviews the preparation or extraction procedure for possible errors, checks the instrument calibration, spike and calibration mixes, instrument sensitivity, and any other potential sources of error. If failure occurs and an error is identified, the analyst should re-run quality control and RFS samples in the entire analytical batch to confirm the results. Because external QC samples are collected and prepared during the survey and provided to the contractor or grantee laboratory, a single rerun to confirm results is sufficient when all other QC samples are within acceptance criteria. For analyses conducted onboard, if the problem persists or cannot be identified, the matter must be referred to the Chief Scientist for further investigation. Depending upon the Chief Scientist's evaluation, the analyst may or may not be required to prepare and re-run the samples again. Additionally, if the results are significantly different than the expected concentrations based on historical data or related samples, then the analyst may split the RFS sample in

the laboratory and analyze the splits. Once a decision is made, full documentation of the corrective action procedures and assessment of the final result must be filed with the WQS QM Technical Lead (Marvin Palmer) or the GLNPO QM. For analyses conducted at contract or grantee laboratories, this information can be included with submitted data. When contractor or grantee laboratories have a question regarding acceptable corrective actions, they should contact the Biology Technical Lead or Limnology Technical Lead as appropriate for instruction at a time when corrective action can still be taken.

9.7 Data Reporting/Recording

- 9.7.1 When corrective actions are not feasible or do not resolve QC failure, the analyst is responsible for identifying all failed QC samples and RFS samples. If analyses are being conducted onboard, the analyst should document the QC information on the hard-copy Field Information Recording Forms (Appendix H). If analyses are being conducted by contract or grantee laboratories, the analyst should document all QC information with the submitted data.

10.0 WASTE DISPOSAL

- 10.1 The effluent from the chloride channel contains mercuric thiocyanate, which is toxic. This waste should be collected and discarded in the orange labeled (corrosive) waste container.
- 10.2 The effluent from the silica channel is an acidic waste and should be disposed of in the yellow labeled (acidic) waste container.

11.0 PREVENTATIVE MAINTENANCE

- 11.1 Required maintenance is described in the Lachat Procedural SOP.

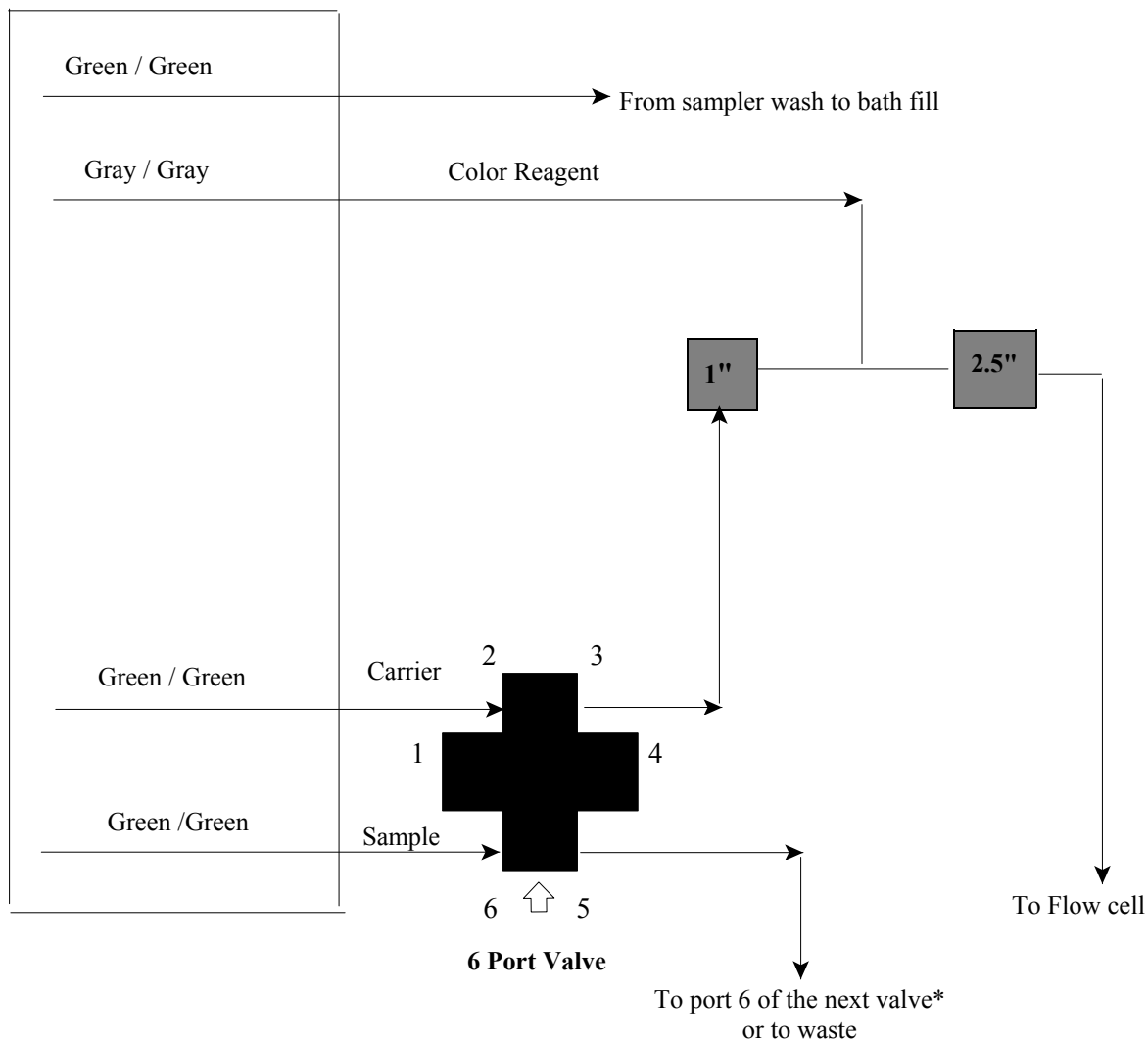
12.0 TROUBLESHOOTING

- 12.1 The most common problem is air bubbles in the lines due to insufficient purging of reagents with helium.

13.0 REFERENCES

- 13.1 Lachat Instruments, Method Number 10-117-07-1-B, Chloride in waters, Revision Date September 1994.
- 13.2 Lachat Instruments, Method Number 10-114-27-1-A, Silica as silicon dioxide (SiO₂), Revision Date September 1998.

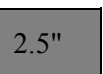
14.0 CHLORIDE ANALYTICAL MANIFOLD



Legend



- 1" Mixing coil (there is 70 cm of tubing on the 1.0" coil support)

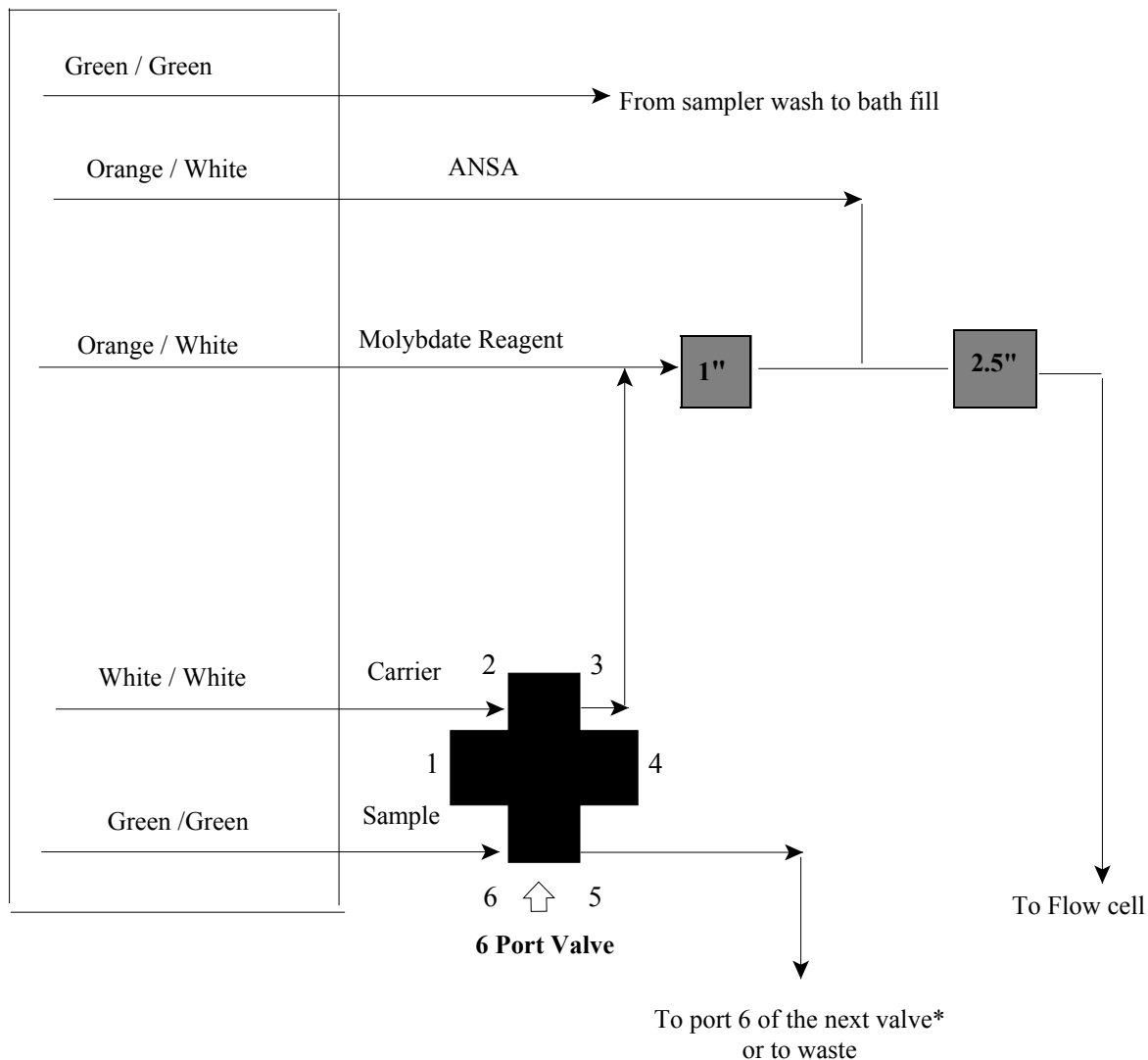


- 2.5" Mixing coil (there is 168 cm of tubing on the 2.5" coil support)

Comments

1. Filter used is 480 nm.
 2. Sample loop length is 100 cm. (0.032") ID.
 3. All manifold tubing is 0.032" ID. This related to a flow of 5.2 uL/cm.
 4. The **carrier** is helium degassed reagent water.
- * If more than one channel is being used.

15.0 SILICA ANALYTICAL MANIFOLD



Legend



- 4" Mixing coil (there is 225 cm of tubing on the 4.0" coil support)

Comments

1. Filter used is 820 nm.
 2. Sample loop length is 50 cm. (0.022") ID.
 3. All manifold tubing is 0.022" ID. This related to a flow of 2.5 uL/cm.
 4. The **carrier** is helium degassed reagent water.
- * If more than one channel is being used.